

JP Kokai Hei 9-110405

(54) [Title of the Invention] Aluminum Nitride and Device for
Producing a Semiconductor

(57) [Abstract]

[Object] To reduce the lightness of an aluminum nitride and to make the color nearly black without adding a metal compound such as a sintering aid or a blackening agent, especially a heavy metal compound, to the aluminum nitride.

[Solution] A g-value of an unpaired electron of the aluminum nitride in a spectrum by an electron spin resonance method is 2.0010 or more, preferably 2.0040 or more. Aluminum-aluminum bonds are formed in a main crystal phase of the aluminum nitride. The aluminum nitride has a auxiliary crystal phase made of AlON besides the main crystal phase. Or a spin amount per unit mg of the aluminum in a spectrum of the aluminum nitride by an electron spin resonance method is 5×10^{12} spin/mg or less.

[Claims]

[Claim 1] An aluminum nitride, wherein a g-value of an unpaired electron of the aluminum nitride in a spectrum by an electron spin resonance method is 2.0010 or more.

[Claim 2] The aluminum nitride according to claim 1, wherein said g-value is 2.0040 or more.

[Claim 3] The aluminum nitride according to claim 1 or 2 which comprises the main crystal phase, and an auxiliary crystal phase made of AlON.

[Claim 4] The aluminum nitride according to any of claims 1 to 3 which is substantially free of an $(\text{AlN})_x(\text{Al}_2\text{O}_3)_{1-x}$ phase and has a lightness specified in JIS Z 8721 of N4 or less.

[Claim 5] A device for producing a semiconductor, wherein the aluminum nitride according to any of claims 1 to 4 is used as a substrate.

[Claim 6] An aluminum nitride, wherein a spin amount per unit mg of the aluminum in a spectrum of the aluminum nitride by an electron spin resonance method is 5×10^{12} spin/mg or less.

[Detailed Description of the Invention]

[0001]

[Technical Field] The present invention relates to an aluminum nitride and a device for producing a semiconductor using the aluminum nitride as a substrate.

[0002]

[Prior Art] In devices for producing a semiconductor such as etching devices or chemical gas phase growing devices, so-called stainless heaters or indirect-heating type heaters have been generally used.

However, when such heat sources were employed, particles sometimes have been produced by the action of a halogen-based corrosive gas and a heat efficiency was poor. In order to solve those problems, the present applicant disclosed a ceramic heater in which a wire made of a high melting point metal is buried inside a dense ceramic substrate (JPKokaiHei 3-261131). This wire is spirally coiled inside the discoidal substrate, and terminals are connected to the opposite ends of the wire. It was found that such a ceramic heater has excellent characteristics particularly suitable for use in the manufacturing of semiconductors.

[0003] It is considered that nitride-based ceramics such as silicon nitride, aluminum nitride, and sialon are preferred as ceramics constituting substrates for the ceramic heaters. Further, in some cases, a susceptor is placed on the ceramic heater, and a semiconductor wafer placed on the susceptor is heated. The present applicant disclosed that aluminum nitride is preferred as substrates for such ceramic heaters and susceptors (JPKokaiHei 5-101871). Particularly in the device for producing a semiconductor, halogen-based corrosive gases such as ClF_3 gas are often used as an etching gas or a cleaning gas because of the confirmation that aluminum nitride has extremely high corrosion resistance against such halogen-based corrosive gases.

[0004]

[Problems which the Invention is to Solve] An aluminum nitride sintered body itself generally is white or whitish gray. However, it is desired that the substrate to be used as the above-mentioned heater or susceptor

is black, because the black substrate has a greater radiation heat capacity and a better heating characteristic as compared with the white ones. Further, if the white or gray substrate is used in such products, uneven color is unfavorably likely to appear at the surface thereof. Therefore, some improvement has been demanded.

Furthermore, customers prefer blackish brown, or blackish gray substrates and the like having a high black degree and a low lightness than the whitish or gray substrates. In addition, the whitish or gray substrates are also poor in the radiation characteristics.

[0005] In order to make an aluminum nitride sintered body black, it is known that by adding an appropriate elementary metal (a blackening agent) to a powdery raw material, a black aluminum nitride sintered body is produced after firing the resulting mixture (JP Kokou Hei 5-64697). As the additive, tungsten, titanium oxide, nickel, vanadium and the like are known.

[0006] However, if an elementary metal is incorporated into an aluminum nitride sintered body as a blackening agent, the content of metallic impurities in the aluminum nitride sintered body naturally becomes larger due to the addition of the additive. Particularly, if a Ia group element, a IIa element and/or a transition metal element exists in the aluminum nitride sintered body in the semiconductor manufacturing process, such element(s) adversely afford serious problem upon the semiconductor wafer or the device for producing a semiconductor itself, even if the content is very small (for example, this may cause a defect in the semiconductor). Therefore, it has

been demanded to decrease the lightness of the aluminum nitride sintered body without adding the above blackening agent thereinto.

[0007] An object of the present invention is to reduce the lightness of an aluminum nitride and to make the color nearly black without adding a metal compound such as a sintering aid or a blackening agent, especially a heavy metal compound, to the aluminum nitride. Another object of the present invention is to provide a device for producing a semiconductor having a high radiation efficiency and a high commercial value by using a substrate with such an increased degree of black.

[0008]

[Means for Solving the Problems] An aluminum nitride according to the present invention is characterized in that a g-value of an unpaired electron of the aluminum nitride in a spectrum by an electron spin resonance method is 2.0010 or more.

[0009] Moreover, the aluminum nitride according to the present invention is characterized in that a spin amount per unit mg of the aluminum in a spectrum of the aluminum nitride by an electron spin resonance method is 5×10^{12} spin/mg or less.

[0010] Furthermore, the present invention is characterized in that the above-mentioned aluminum nitride is used as a substrate in a device for producing a semiconductor.

[0011] The present inventors, in the process of studying the aluminum nitride sintered body, successfully produced blackish gray or blackish brown aluminum nitride sintered bodies which are almost free of metal

elements other than aluminum such as blackening agents, further are significantly low in the lightness as specified in JIS Z 8721 of N4 or less.

[0012] Since such the aluminum nitride has black color of a lightness specified in JIS Z 8721 of N4 or less, thereby provides high heat radiation capacity and has a high heating characteristics. Therefore, it will be a suitable substrate for forming heat materials of ceramic heaters and susceptors. In addition, it is possible to make it contain very little metal elements other than aluminum, there is no possibility of contaminating semiconductors. Particularly, the aluminum nitride according to the present invention has no adverse effect on semiconductor wafers or devices itself in semiconductor manufacturing processes. Irregular color of its surface, if any, is almost negligible. Thus the aluminum nitride sintered body has an excellent appearance and further has high blackness, resulted in significantly improved commercial value.

[0013] The term "lightness" will be described herein. The surface color of an object is represented by the three color perception attributes: hue, lightness and chromaticness. The lightness represents the degree of visible reflection from the object. Indication manner for the degree of these three attributes is specified in JIS Z 8721. The lightness V is given with reference to achromatic color, and therefore the lightness of ideal black is 0 and that of ideal white is 10. The lightness range of each color from ideal black to ideal white is divided into 10 parts each having the same visual

brightness rate and numbered consecutively from N0 to N10. In practically determining the lightness of the aluminum nitride, its surface color is compared with each of the standard color chips. In principle, the lightness is given to the first decimal place, and 0 or 5 is put in the decimal place.

[0014] The present inventors have investigated the factors attributable to high-grade black and low lightness in the aluminum nitride obtained as described below. As a result, it was found that if the aluminum nitride meets specific conditions as described below, it can be blackened progressively and poor in lightness. Based on such a result, the present invention has been completed.

[0015] First, the aluminum nitride having a lightness of 4 or less and being blackish brown or blackish gray were analyzed by X-ray diffraction. As a result, it was found that AlON was generated as the auxiliary crystal phase although the main crystal phase was AlN. In such aluminum nitride samples, typically, AlON particles having a diameter of 0.1 μm order were formed in AlN crystal particles having a diameter of 1 to 3 μm . For example, under the conditions described below, from a sample produced by sintering an aluminum nitride powder having a purity of 99.9% by weight or more at 1750°C to 1900°C, blackish brown or blackish gray samples having a lightness of N3 to N4 were obtained. On the other hand, from an aluminum nitride produced by sintering an aluminum nitride powder having a purity of 99.9% by weight or more at 1950°C, yellow-white sample was obtained.

[0016] When the crystal structure of the sample obtained by sintering

at 1950°C was analyzed, so-called 27R phase (Al_2O_3 -7 (AlN) phase) was formed other than the AlN main crystal phase. The AlN crystal phase had a particle diameter of about 2 to 4 μm , and the above-mentioned 27R phase was precipitated at the boundaries of the AlN grains. According to the known Al_2O_3 -AlN phase diagram, the crystal phase which generates after sintering changes between above and below the border of 1920°C. Therefore, the above-mentioned difference in the crystal phase is supposed to be caused by the difference of the sintering temperature.

[0017] By heating the above-mentioned low lightness samples at 1900°C under nitrogen atmosphere, the blackish brown or blackish gray portions disappeared and gray and yellow-white portions were generated. In the gray portions, a spherical AlON crystal phase and Al_2O_3 -AlN phase were formed. The yellow-white portion had little 27R phase but mainly the spherical AlON phase. Regardless of the color tone, the aluminum nitride had no difference in AlN lattice constant. In other words, no specific correlation was found between the type of the non-AlN crystal phase and the color tone or the lightness. Therefore, the change in the color tone of the aluminum nitride is supposed to be caused by the defect structure in the AlN crystal phase and at the grain boundary rather than by the type of the crystal phase.

[0018] The inventors measured the spectrum by electron spin resonance (ESR) method of the above-mentioned each sample in order to reveal the structure of the defects in the AlN crystal phase and at the grain boundary. The principle will be briefly described below. By

the Zeeman effect, the energy level of an unpaired electron is separated under a certain magnetic field. The interaction of the orbital motion of the electron and the nuclear magnetic efficiency of the atoms in the vicinity sensitively changes in response to this energy level. The ESR method provides information about the atoms in the vicinity of the atom having unpaired electron atoms, the chemical bonds and the like through the measurement of the separated energy level.

[0019] The above-mentioned black samples in lightness of 4 or less and the gray or the yellow-white portions obtained by heating thereof were measured for ESR spectrum. In the aluminum nitride, the spin amount of the unpaired electron of aluminum changes by the crystal field in which the unpaired electron exists. The spin amount of free electrons is 2.0000 in theoretical value, and 2.002316 in relativistic correction value (g). In the AlN crystal phase, the Al and N atoms form a tetradentate wurtzite structure and an aluminum atom and three nitrogen atoms form an sp^3 hybrid orbital. The spin amount value of each sample provides information about the type of the crystal coordination for the unpaired electron in the lattice defects and the type of the elements around the unpaired electron.

[0020] Fig. 1 shows an ESR spectrum of the above-mentioned blackish brown aluminum nitride; Fig. 2 shows an ESR spectrum of the gray portion; and Fig. 3 shows an ESR spectrum of the yellow-white portion. Referring to these data, the blackish brown aluminum nitride had a g-value in spin amount of 2.0053 ± 0.0001 and showed a sharp peak of high intensity. The spin amount per unit mg of this aluminum was

7.9×10^{11} spin/mg. The gray portion had a g-value of 2.0018 ± 0.0001 with low peak intensity. The spin amount per unit mg of aluminum was 2.1×10^{12} spin/mg. The yellow-white portion had a g-value of 1.9978 ± 0.0001 and showed a broad peak of high intensity. The spin amount per unit mg of the aluminum was 1.5×10^{13} spin/mg.

[0021] The spin amount (g-value) of the unpaired electron significantly changes with the type of the atom coupled to the Al atom having the unpaired electron. The significant change of the g-value as described above is attributable to the change of the type of the atom coupled to the aluminum. Specifically, the g-value significantly changes, as the type of this coupled atom changes nitrogen to carbon or aluminum atom. A similar change of the spin amount is reported on the four-coordinate Si atom (see "ESR Evaluation of Materials", Industrial Publishing & Consulting, Inc., p.57). The significant change of the g-value obtained by this measurement would be attributed to change of type of the four-coordinate atom to the aluminum atom, and there should be aluminum to aluminum bonds.

[0022] That is, as shown in Fig. 4, the g-value increases and the half band width decreases (the peak becomes sharper and its width becomes smaller) as the three-coordinate nitrogen atoms are gradually substituted with aluminum atoms.

[0023] It can be understood that the g-value changes with the number of the Al-coordinate nitrogen atoms. It is presumable that the nitrogen atoms are substituted with carbon or oxygen atoms because carbon and oxygen atoms are contained in the AlN crystal phase. The

rate of substitution with these atoms, however, should be very small, because the g-value decreases by such substitution.

[0024] As stated above, the yellow-white portion has a peak g-value of less than 2.00 and shows a broad peak with a large half band width. In such samples, it is supposed that oxygen is dissolved in the AlN crystal solid, specifically, the N^{3+} site is substituted with O^{2-} and Al^{3+} is lost. And the unpaired electron trapped in the lattice defect may form a color center and effectively absorb visible light in a short wave range to develop color yellow-white. Or the N^{3-} may also be substituted with two oxygen ions and a color center of O^{2-} may be formed.

[0025] On the contrary, the blackish brown sample has a high peak g-value and shows a sharp peak. The blackish gray sample gives similar results and the slight difference in color tone at the lightness level of 4 or less is not substantial. In such less lightness aluminum nitride samples, aluminum-aluminum bonds are formed, which is supposed to have metallic bond-like characteristics so that they can absorb a wide continuous wave range of visible light. This is attributable to the decrease of lightness of the aluminum nitride.

[0026] In addition, it has been found that each electric resistance of the blackish brown sample and blackish gray sample is two order of magnitude higher than that of the yellow-white sample. Comparing the absorption peaks in the ESR spectrum of each sample, the yellow-white sample has the highest absorption intensity and also has wide half band width. This can be supposed that a largest number

of conduction electrons should be trapped or captured in the above-mentioned lattice defects of the color center and such conduction electrons trapped should attribute to the decrease in the electric resistance.

[0027] Other different samples were also measured for ESR spectra in the same manner as mentioned above, and as a result, it was confirmed that it is necessary to make a g-value of 2.0040 or more for blackish brown or blackish gray materials (with a lightness of 4 or less). For more stable production of the less lightness samples, a g-value is more preferably made to be 2.0050 or more.

[0028] Among the above-mentioned samples, for the gray portions formed by heat treatment of the blackish brown sample, the ESR spectrum as shown in Fig. 2 was obtained and the g-value was 2.0018 ± 0.0001 . This is a slightly lower g-value than that of the blackish brown samples, but was relatively high as compared with that of the conventional white or opaque white aluminum nitride or the above-mentioned yellow-white aluminum nitride, and the relative decrease in the lightness was microscopically confirmed.

[0029] However, in this sample, a small amount of the $(\text{AlN})_x(\text{Al}_2\text{OC})_{1-x}$ phase was also found to be generated. It was found that around this crystal phase, micro gaps or voids (micro spaces) were formed between the AlN crystal phase and that light is scattered in these voids, which causes the increase of the lightness. Accordingly, the effect of the present invention can be confirmed in such matrixes. However, the aluminum nitride is preferably prevented from having the

$(\text{AlN})_x(\text{Al}_2\text{O}_3)_{1-x}$ phase so that the lightness can be more effectively reduced to 4 or less, further to 3.5 or less.

[0030] Fig. 5 shows a microstructure of the above-mentioned blackish brown aluminum nitride. As shown in Fig. 5, micro AlON crystals exist in the AlN crystal grains, and the grain boundary portions at which the crystals are in contact with each other have a dense void-free state. Fig. 6 is an electron micrograph showing a magnified grain boundary portion composed of the AlN crystal for the blackish brown aluminum nitride sample. The AlN crystal boundary has no heterogeneous phase.

[0031] In addition, aluminum nitride sintered bodies of dense and black meeting the object of the present invention were obtained when they had a spin amount per unit mg of aluminum of 5×10^{12} spin/mg or less in their electron spin resonance spectra. From this viewpoint, preferred spin amount per unit mg of aluminum was 1×10^{12} spin/mg or less, which substantially corresponded to a g-value of 2.0040. The practical spin amount per unit mg of aluminum is preferably 1.0×10^{10} spin/mg or more, more preferably 1×10^{11} spin/mg or more.

[0032] The spin amount was measured according to the method described in Hiroaki Oya and Atsushi Yamauchi, "Electron Spin Resonance", Kodansha Ltd. The absorption intensity of the ESR spectrum is proportional to the rate of the an unpaired electron in the aluminum nitride crystal particles. The determination of the g-value needs to be made in comparison with the known g-values of the standard samples. Specifically, the samples with known g-values and the

aluminum nitride sintered body samples according to the present invention should be measured under the same conditions, and the resulting absorption curves should be converted into integral curves on which the areas are compared with each other.

[0033] The present inventors used a TEMPOL (4-hydroxy-2,2,6,6-tetramethylpiperidine-1-oxyl) solution with a known spin amount and determined a hyperfine line of $\text{Mn}^{2+}/\text{MgO}$, and then compared the spin amounts with each other through the line to calculate a spin value from the peak area ratio.

[0034] The less lightness aluminum nitride according to the present invention is preferably produced as follows. As the raw material, an aluminum nitride powder produced by reducing nitriding is preferably used. Addition of metal elements other than aluminum to the raw material of aluminum nitride powder should be avoided, and the concentration of such metal elements in the raw material is preferably 100 ppm or less. In the description, the "metal elements other than aluminum" include the metals belonging to Ia to VIIa, VIII, Ib, and IIb groups in the periodic table, and some of the metals belonging to the IIIb and IVb groups in the periodic table such as Si, Ga and Ge.

[0035] Preferably, high-purity aluminum nitride powder is prepared by a reducing nitriding process as mentioned above, and the aluminum nitride powder is formed into a formed body by uniaxial pressing or cold isostatic pressing method. The formed body is included or encapsulated into a carbon coating and fired, being kept from contact

with air. The firing process can include hot pressing or hot isostatic pressing.

[0036] The formed body may have such a shape as shown in Fig. 8 to be included in the carbon coating. Specifically, foils 5A and 5B made of graphite are respectively placed on the upper and lower faces of the formed body 6 when the formed body 6 is placed between an upper punch 1A and a lower punch 1B. The formed body 6 and a pair of the foils 5A and 5B are placed between each of the spacers 4A and 4B, respectively. At the same time, a foil 7 made of graphite is placed so as to cover both sides of the formed body 6. The formed body 6 is sealed into the assembly of the graphite foils 5A, 5B and 7. The formed body 6 and the foil 7 are placed in a die 9 made of carbon with a sleeve 8 made of carbon interposed. A pressing machine is driven to give heat and forces in the vertical directions in Fig. 8 by means of the upper and lower punches 1A and 1B.

[0037] The process, in which the formed body was sealed into the high carbon or carbon compound content material coating and heated and pressed under the above-mentioned conditions and controlled atmosphere as described below, provided a sintered body which had the aluminum-aluminum bonds as mentioned above and continuous visible light absorption characteristics.

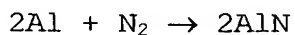
[0038] The firing temperature may be from 1750°C to 1900°C. The pressure in the firing is 100 kg/cm² or more, preferably 150 kg/cm² or more, and more preferably 200 kg/cm² or more. However, in terms of the performance of practical machines, 0.5 ton/cm² or less is

preferred.

[0039] The present inventors have further carefully examined the processes and concluded as follows. Known processes for preparing aluminum nitride powder include a reducing nitriding process and a direct nitriding process. Each process works according to the following formula.

Reducing Nitriding Process: $\text{Al}_2\text{O}_3 + 3\text{C} + \text{N}_2 \rightarrow 2\text{AlN} + 3\text{CO}$;

Direct Nitriding Process: $\text{Al}(\text{C}_2\text{H}_5)_3 + \text{NH}_3 \rightarrow \text{AlN} + 3\text{C}_2\text{H}_6$ (Gas Phase Process)

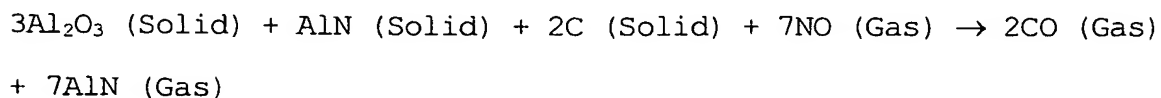


[0040] As shown above, the aluminum nitride crystal obtained by the reducing nitriding process is produced through the reducing nitriding reaction of $\gamma\text{-Al}_2\text{O}_3$ phase with carbon. It is considered that the carbon used as a reducing catalyst is left on the surface of the aluminum nitride crystal, and unreacted oxygen is left in the aluminum nitride. The aluminum nitride is thermodynamically unstable in the air. Particularly, the surface-active fine powder for sintering easily reacts with the atmospheric moisture or oxygen at room temperature and oxygen content increases. Thus, oxides or hydroxides are used to cover the surface oxide layer and stabilize the active aluminum nitride crystal against the moisture and oxygen. This oxidation process is also used after the reducing process for removing the remaining carbon atoms from the particle surface to increase purity.

[0041] In this regard, the key factors for the quality of the aluminum nitride crystal are the oxide film on the particle surface and the

amount of oxygen dissolved in the aluminum nitride crystal solid in the reducing nitriding process.

[0042] As described above, when the particles produced by reducing nitriding are sealed into the carbon coating and heated under pressure away from the oxidative atmosphere such as air, the atmosphere inside the coating becomes important. On the surfaces of the aluminum nitride particles, alumina films exist. For example, the sintering is carried out with a reducing atmosphere (nitrogen gas atmosphere) inside the coating made of graphite foil under a pressure of 250 kg/cm² at a temperature of 1850 to 1950°C. The partial pressure of oxygen is in the order of ppm. In the sintering, in the vicinity of the surface of the aluminum nitride particle, Al₂O₃ remaining on the surface reacts with C (carbon) to form CO gas. In this reaction, the species of the gas phase include Al, AlO, Al₂O, Al₂O₂, AlC, AlC₂, Al₂C₂, AlN, NO and CO.



[0043] The equilibrium partial pressure of each gas phase species is calculated on the assumption that the partial pressure of CO in the sintered body is constant, a graph represented in Fig. 9 is obtained. As shown in the graph, the partial pressure decreases in the order of AlN, Al and Al₂O. The carbon allows the reduction of Al₂O₃ and AlN is generated. Also, as can be seen from the partial pressures of Al and Al₂O, the AlON (AlN+Al₂O) phase containing Al-Al bonds and oxygen is presumed to be produced in the crystal lattice. The

observation with TEM showed that the Al_2O_3 layer existed at the crystal grain boundary. The Al_2O_3 layer should be in the form of $(\text{C} + \text{Al}_2\text{O}_3)$ produced by the coupling of the carbon remaining on the surface of the aluminum nitride particles to Al_2O_3 in the gas phase species.

[0044] At a temperature of 1950°C or below, the Al species has a higher partial pressure than that of Al_2O_3 species, but the order is reversed at a temperature above 1950°C . Namely, at a higher sintering temperature, the production of the Al_2O_3 phase would be enhanced. On the other hand, Al-Al bonds would be formed at 1950°C or below.

[0045] For the color tone of the AlN crystal, the defect structure in the crystal is important, and as described above, such a defect structure is primarily affected by the oxygen content in the powdered raw material, the atmosphere for the sintering, and the gas phase species generated in the sintering process. As stated above, particularly important are the effect of oxygen and the carbon atoms remaining on the surface of the aluminum nitride particles and the role of the carbon supplied from the graphite foil to the atmosphere. And as described above, the oxide is supposed to be reduced with the carbon, and the reduction should lead to the generation of the AlN phase, Al phase, AlO_2 phase, AlON phase, and Al-Al bonds.

[0046] For stable production of the less lightenss aluminum nitride sintered body, the above-mentioned process preferably uses a pressure of 150 kg/cm^2 or more, more preferably 200 kg/cm^2 or more.

[0047] Incidentally, the relative density of the aluminum nitride is a percent value defined by the formula: Relative Density = Bulk

Density/Theoretical Density.

[0048] The aluminum nitride according to the present invention provides high heat radiation capacity and has high heating properties. Irregular color of its surface, if any, is almost negligible, and color blackish brown or blackish gray provides a high commercial value. Thus, it can be used particularly preferably for various types of heating device. Further, the present aluminum nitride is free of sintering aids or blackening agents, which are to be the source of metal elements other than aluminum. The content of metal atoms other than aluminum can be made to 100 ppm or less, thereby provides no risk of contamination. Thus, it is most suitable for high purity process materials. Particularly, it has no serious effect on semiconductor wafers or equipment itself in the semiconductor processes.

[0049] Example of a device for producing a semiconductor in which the aluminum nitride according to the present invention is used as a substrate include active type devices such as a ceramic heater in which a resistance heating element is embedded into the substrate, a ceramic electrostatic chuck in which an electrode for electrostatic chuck is embedded into the substrate, a heater with electrostatic chuck in which the resistance heating element and the electrode for electrostatic chuck are embedded into the substrate, and a radio-frequency generating electrode device in which a plasma generating electrode is embedded into the substrate.

[0050] Furthermore, examples of the above-mentioned device for

producing a semiconductor also include a susceptor for placing a semiconductor wafer, a dummy wafer, a shadow ring, a tube for generating a radio-frequency plasma, a dome for generating a radio-frequency plasma, a radio-frequency transparent window, an infrared-ray transparent window, a lift pin for supporting a semiconductor wafer, and a shower plate.

[0051] The aluminum nitride preferably have a thermal conductivity of $90 \text{ W/m} \cdot \text{K}$ or more particularly for use in a substrate for heating member of a ceramic heater, a heater with electrostatic chuck, a susceptor for holding a semiconductor or the like.

[0052]

[Examples] (Experiment A)

An aluminum nitride sintered body was produced as follows. As the raw material, high-purity aluminum nitride powder prepared by reducing nitriding or direct nitriding was used. Each powder had a Si, Fe, Ca, Mg, K, Na, Cr, Mn, Ni, Cu, Zn, W, B, or Y content of 100 ppm or less, and metals other than aluminum were detected.

[0053] Each raw material powder was uniaxially pressed to form a pre-formed body in a circle plate shape. As shown in Fig. 8, the formed body 6 was placed in the die and sealed into the carbon foil as described above, and then fired by hot pressing process under a pressure of 200 kg/cm^2 at 1900°C for 2 hours, thereby obtaining an aluminum nitride sample named A1.

[0054] The sample A1 was heated under nitrogen atmosphere at 1900°C for 2 hours to form a sample A2, which had a yellow-white peripheral

portion containing a gray portion therein. The sample A1 and the yellow-white and gray portions of the sample A2 were each measured for an ESR spectrum. Fig. 1 is the ESR spectrum of the sample A1, Fig. 2 is the gray portion of the sample A2, and Fig. 3 is the yellow-white portion of the sample A2. Spin amount of the sample A1 had a g-value of 2.0053 ± 0.0001 and showed a sharp peak of high intensity. The spin amount per unit mg of the aluminum was 7.9×10^{11} spin/mg. The gray portion had a g-value of 2.0018 ± 0.0001 and showed low peak intensity. The spin amount per unit mg of the aluminum was 2.1×10^{12} spin/mg. The yellow-white portion had a g-value of 1.9978 ± 0.0001 and showed a broad peak of high intensity. The spin amount per unit mg of the aluminum was 1.5×10^{13} spin/mg.

[0055] The sample A1 had a lightness of N3.5, the yellow-white portion of the sample A2 had N8, and the gray portion of the sample A2 had N5. Further, each sample was measured for the main crystal phase and the other crystal phases by X-ray diffraction analysis, and the results as described above were obtained.

[0056] Of these results, an electron micrograph of the ceramic structure of the sample A1 is shown in Fig. 5, and an electron micrograph of the ceramic structure in the vicinity of the grain boundary of the aluminum nitride particle in the sample A1 is shown in Fig. 6. The ceramic structure of the gray portion is also shown in Fig. 7. As regards this structure, the X-ray diffraction analysis and the visible light absorption spectrum analysis of the matrix portion provided the same results as those of the sample A1. However, the

matrix contained a black $(\text{AlN})_x(\text{Al}_2\text{O}_3)_{1-x}$ phase, and between this crystal particle and the AlN crystal phase, a little void was observed, which scattered light and shined white. The matrix structure of the sintered body was basically of the aluminum nitride of the present invention, and the blackening was relatively proceeding. However, the above-mentioned scattered light increased the lightness of the sintered body to N5.

[0057] (Experiment B) In a similar manner to Experiment A, the aluminum nitride sintered bodies of Experiment B1 to B9 in Tables 1 and 2 were prepared. As the raw material, high-purity aluminum nitride powder prepared by reducing nitriding or direct nitriding was used. Each powder had a Si, Fe, Ca, Mg, K, Na, Cr, Mn, Ni, Cu, Zn, W, B, or Y content of 100 ppm or less, and no other metals other than aluminum were detected.

[0058] In each of the Experiment, different temperatures and pressures were used in the firing process as shown in Tables 1 and 2. The holding time in the firing process was set to 2 hours. Each aluminum nitride sintered body of each experiment was measured for the main crystal phase and the other crystal phases by X-ray diffraction analysis. Each sintered body was also measured for relative density, color tone and lightness. The relative density of the sintered body was calculated by dividing the bulk density by the theoretical density. The bulk density was measured by the Archimedes' method. The theoretical density of the sintered body is 3.26 g/cc because the density is free of any high-density sintering aid. The color tone

of the sintered body was visually measured, and the lightness was measured by the method described above.

[0059]

[Table 1]

	Experiment B1	Experiment B2	Experiment B3	Experiment B4	Experiment B5
AlN Powder	Reducing Nitriding	Reducing Nitriding	Reducing Nitriding	Reducing Nitriding	Reducing Nitriding
Firing Temperature (°C)	1800	1800	1700	1750	1850
Pressure (kg/cm ²)	200	150	200	150	100
Main crystal Phase	AlN	AlN	AlN	AlN	AlN
Other Crystal phases	ALON	ALON	ALON	ALON	ALON
Relative Density (%)	99.4	99.4	97.8	99.0	99.0
g-Value	2.0052	2.0052	1.9971	2.0051	2.0018
Color Tone of Sintered Body	Blackish Gray	Blackish Gray	White	Blackish Gray	Gray
Lightness of Sintered Body	N3.5	N3.5	N8.0	N4.0	N5.0

[0060]

[Table 2]

	Experiment B6	Experiment B7	Experiment B8	Experiment B9
AlN Powder	Reducing Nitriding	Reducing Nitriding	Reducing Nitriding	Direct Nitriding
Firing Temperature (°C)	1800	1900	1950	1900
Pressure (kg/cm ²)	250	200	200	300
Main crystal Phase	AlN	AlN	AlN	AlN
Other Crystal phases	AlON	AlON	AlON	AlON
Relative Density (%)	100	99.7	99.4	99.0
g-Value	2.0059	2.0053	1.9978	2.0012
Color Tone of Sintered Body	Blackish Brown	Blackish Gray	Yellow-Wh ite	Gray
Lightness of Sintered Body	N2.0	N3.5	N8.0	N5.0

[0061] From the results, it is clear that the g-value of the ESR spectrum shows a significant correlation with the color tone and lightness. Experiments B1, B2, B4, B5, B6, B7 and B9 are in the range of the present invention, but B3 and B8 are not in the range of the present invention.

[0062] (Heat Test on Wafer) The aluminum nitride sintered body of the sample A1 according to the present invention was formed into a plate of 210 mm in diameter and 10 mm in thickness. This plate was placed in a vacuum chamber having a heating mechanism with infrared lamps. On this plate, a silicon wafer of 8 inch in diameter was placed, and thermo-couples were attached to simultaneously measure the both temperatures of the plate and the silicon wafer. To an aluminum reflecting plate, 20 infrared lamps were attached, each having an infrared ray peak around a wavelength of 1 μ m of 500 W. The reflecting plate with the

lamps was placed on the outside of the vacuum chamber.

[0063] The infrared ray radiating from each lamp is directly, or reflected from the plate, passes through a circular quartz window (250 mm in diameter, 5 mm in thickness) provided in the vacuum chamber, and reach the aluminum nitride plate to heat it.

[0064] In this heating system, each lamp was allowed to radiate, then the plate was heated from room temperature to 700°C in 11 minutes and was held at 700°C for one hour. Each lamp was turned off and the plate was allowed to cool slowly. As a result, the electrical power consumption of the infrared lamps was up to 8700 W, and the temperature was stably controlled. Further, the silicon wafer was measured for its temperature, and the wafer had a temperature of 609°C when the plate was held at 700°C.

[0065] (Comparative Heat Test) Aluminum nitride powder with a carbon content of 200 ppm prepared by reducing nitriding process was used and pressed under a pressure of 3 ton/cm² by cold isostatic pressing method to form a formed body in a circular plate shape. The formed body was fired at 1950°C for 2 hours to form a white aluminum nitride sintered body with a density of 99.4%. The sintered body was subjected to heat test in the same manner as mentioned above.

[0066] As a result, the electrical power consumption was up to 10 kW, and the necessary heating time was about 2 minutes longer. And when an up-and-down heat cycle was repeated between room temperature and 700°C, the infrared lamp was easily broken. Further, the silicon wafer was measured for its temperature, it was 593°C when the plate was held at 700°C. The wafer temperature was relatively low as compared with that of the above example according to the present invention.

[0067] (Electrode and Resistance Heater Embedding Test) As in the case of the sample A1 according to the present invention, the above-mentioned aluminum nitride powder was used. In the powder, a coil (resistance heating wire) of a molybdenum wire of 0.5 mm in diameter was embedded, and a molybdenum electrode

in a circular plate shape of 5 mm in diameter and 10 mm in thickness was connected to the coil and embedded in the powder. The embedded body was uniaxially pressed to form a formed body in a circular plate shape. In this process, the coil embedded in the formed body was made to have a spiral shape in planar view. [0068] As shown in Fig. 8, the circular plate shaped formed body was placed in the die as described above, and held under a pressure of 200 kg/cm^2 at 1800°C for 2 hours by hot pressing process to form an aluminum nitride sintered body, in which the above-mentioned resistance heater and the molybdenum electrode were embedded. The resulting molybdenum electrode is useful as an electrostatic chuck electrode or a high-frequency electrode.

[0069]

[Effect of the Invention] As described above, according to the present invention, it is possible to reduce the lightness of an aluminum nitride and to make the color nearly black without adding a metal compound such as a sintering aid or a blackening agent, especially a heavy metal compound, to the aluminum nitride. It is also possible to provide a commercially valuable device for producing a semiconductor having a high radiation efficiency by using such a highly black substrate.

[Brief Description of the Drawings]

[Fig. 1] An ESR spectrum of a blackish brown aluminum nitride sintered body according to the Examples of the present invention.

[Fig. 2] An ESR spectrum of the gray portion obtained by heating the above-mentioned blackish brown aluminum nitride sample under nitrogen atmosphere.

[Fig. 3] An ESR spectrum of the yellow-white portion obtained by heating the above-mentioned blackish brown aluminum nitride sample under nitrogen atmosphere.

[Fig. 4] A schematic diagram for describing the relationship between the coupling state of aluminum to atoms other than aluminum and the g-value of the ESR spectrum.

[Fig. 5] An electron micrograph showing the ceramic structure

of the aluminum nitride sintered body according to the embodiment of the present invention.

[Fig. 6] An electron micrograph showing the ceramic structure in the vicinity of the grain boundary of the AlN crystal phase particle in the aluminum nitride sintered body according to the Examples of the present invention.

[Fig. 7] An electron micrograph showing the ceramic structure in a state that an $(\text{AlN})_x(\text{Al}_2\text{O}_3)_{1-x}$ phase particles are generated between the matrixes composed of AlN crystal phase particle.

[Fig. 8] A schematic sectional view for describing a hot pressing process which is suitable for manufacturing the aluminum nitride sintered body of the present invention.

[Fig. 9] A graph showing the calculated results of the partial pressures of each gas phase species in the vicinity of the aluminum nitride particle surface in the hot pressing process.

[Explanations of Symbols]

1A, 1B: Punch; 4A, 4B: Spacer; 5A, 5B, 7: Graphite Foil; and 8: Sleeve.

[Amended Claims]

[Claim 1] An aluminum nitride, wherein a g-value of an unpaired electron in a spectrum of the aluminum nitride by an electron spin resonance method is 2.0010 or more.

[Claim 2] The aluminum nitride according to claim 1, wherein said g-value is 2.0040 or more.

[Claim 3] The aluminum nitride according to claim 1 or 2, wherein a spin amount per unit mg of aluminum in a spectrum of the aluminum nitride by an electron spin resonance method is 5×10^{12} spin/mg or less.

[Claim 4] An aluminum nitride, wherein a spin amount per unit mg of aluminum in a spectrum of the aluminum nitride by an electron spin resonance method is 5×10^{12} spin/mg or less.

[Claim 5] The aluminum nitride according to claim 3 or 4, wherein a spin amount per unit mg of aluminum is 1.0×10^{12} spin/mg or more.

[Claim 6] The aluminum nitride according to any of claims 1 to 5, wherein a main crystal phase made of aluminum nitride particles and an auxiliary crystal phase made of AlON particles are comprised.

[Claim 7] The aluminum nitride according to any of claims 1 to 6, wherein the aluminum nitride particle forming said aluminum nitride has a particle diameter of 1 to 3 μm .

[Claim 8] The aluminum nitride according to any of claims 1 to 7, wherein an amount of metal elements other than aluminum in a raw material of said aluminum nitride is 100 ppm or less.

[Claim 9] The aluminum nitride according to any of claims 1 to 8, wherein the aluminum nitride is substantially free of an $(\text{AlN})_x(\text{Al}_2\text{O}_3)_{1-x}$ phase and has a lightness specified in JIS Z 8721 of N4 or less.

[Claim 10] A device for producing a semiconductor, wherein the aluminum nitride according to any of claims 1 to 9 is used as a substrate.

[Claim 11] The device for producing a semiconductor according to claim 10 which is selected from the group consisting of: a

ceramic heater in which a resistance heating element is embedded into said substrate; a ceramic electrostatic chuck in which an electrode for electrostatic chuck is embedded into said substrate; a heater with electrostatic chuck in which the resistance heating element and the electrode for electrostatic chuck are embedded into said substrate; and a radio-frequency generating electrode device in which a plasma generating electrode is embedded into said substrate.

[Claim 12] The device for producing a semiconductor according to claim 10 which is selected from the group consisting of: a susceptor for placing a semiconductor wafer; a dummy wafer; a shadow ring; a tube for generating a radio-frequency plasma; a dome for generating a radio-frequency plasma; a radio-frequency transparent window; an infrared-ray transparent window; a lift pin for supporting a semiconductor wafer; and a shower plate.

1 / 3
DRAWINGS

Fig.1

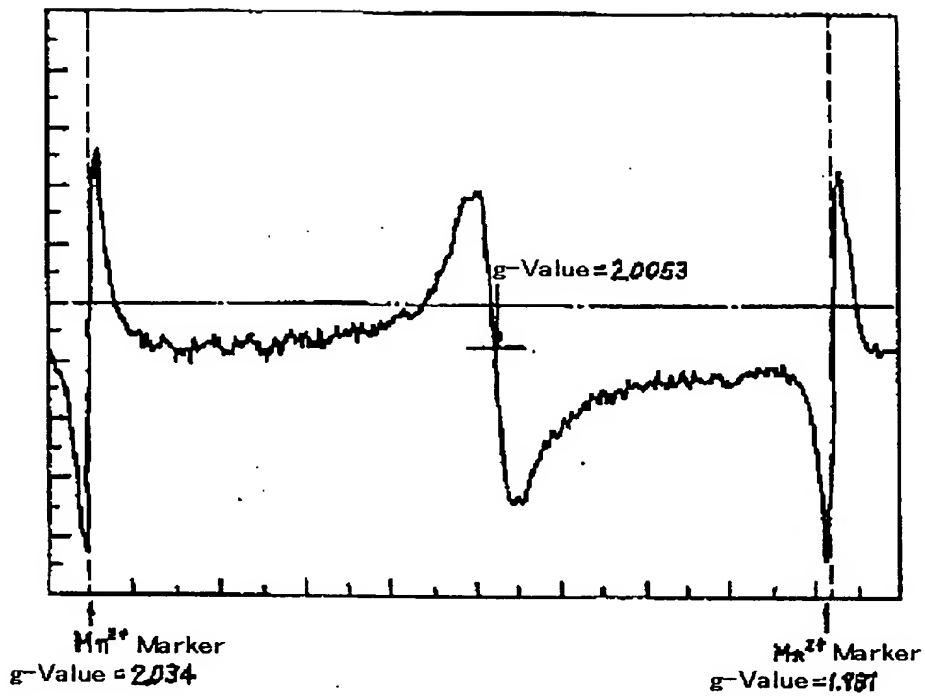


Fig.2

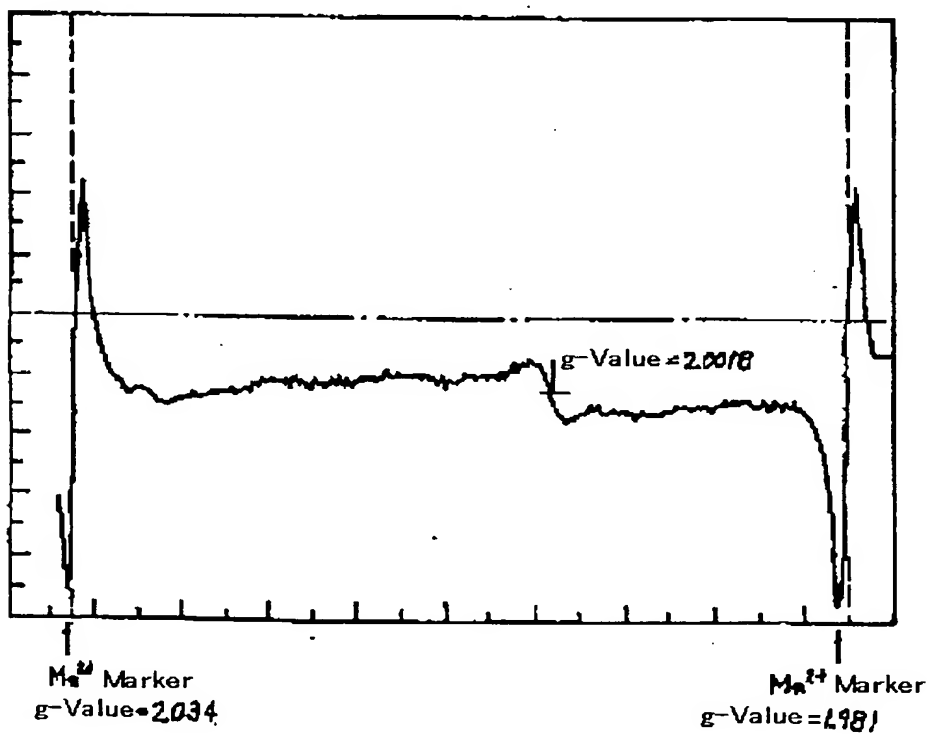


Fig. 3

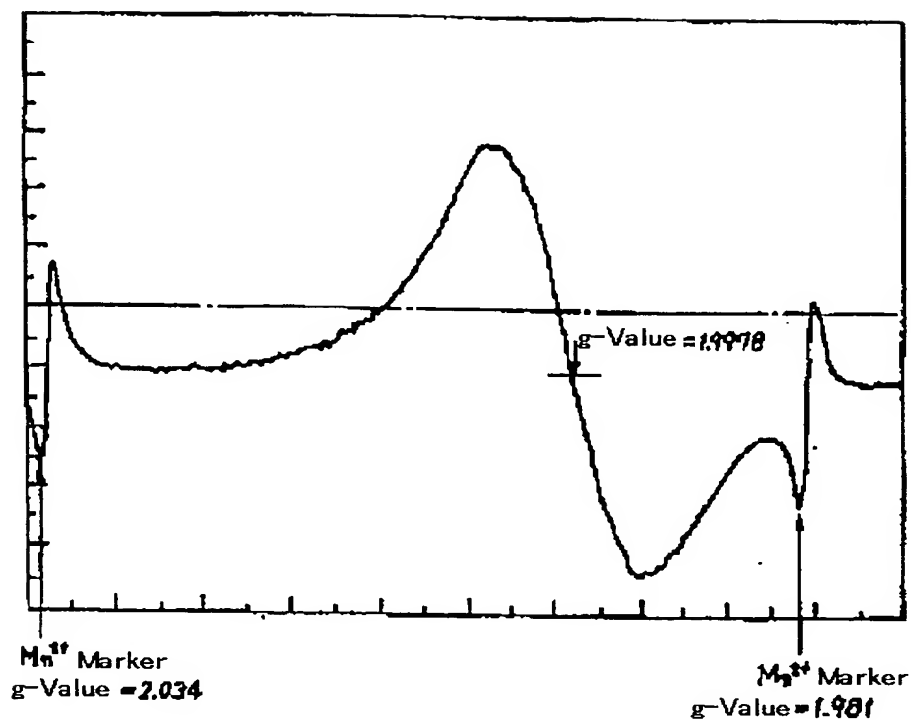


Fig. 4

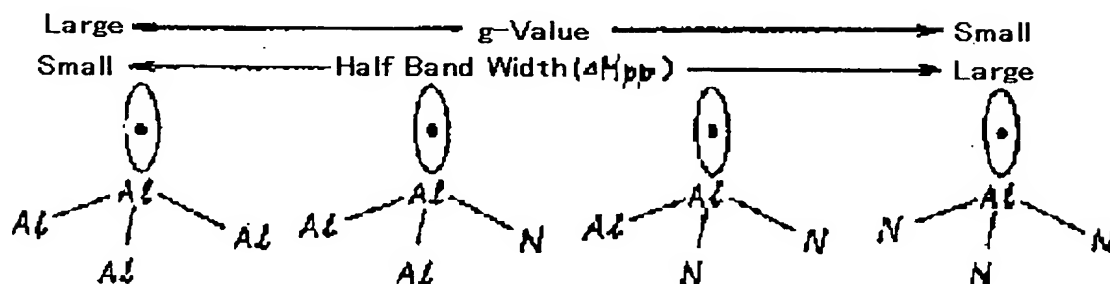


Fig. 5

Photograph Substituted for Drawing

Fig. 6

Photograph Substituted for Drawing

Fig. 7

Photograph Substituted for Drawing

Fig.8

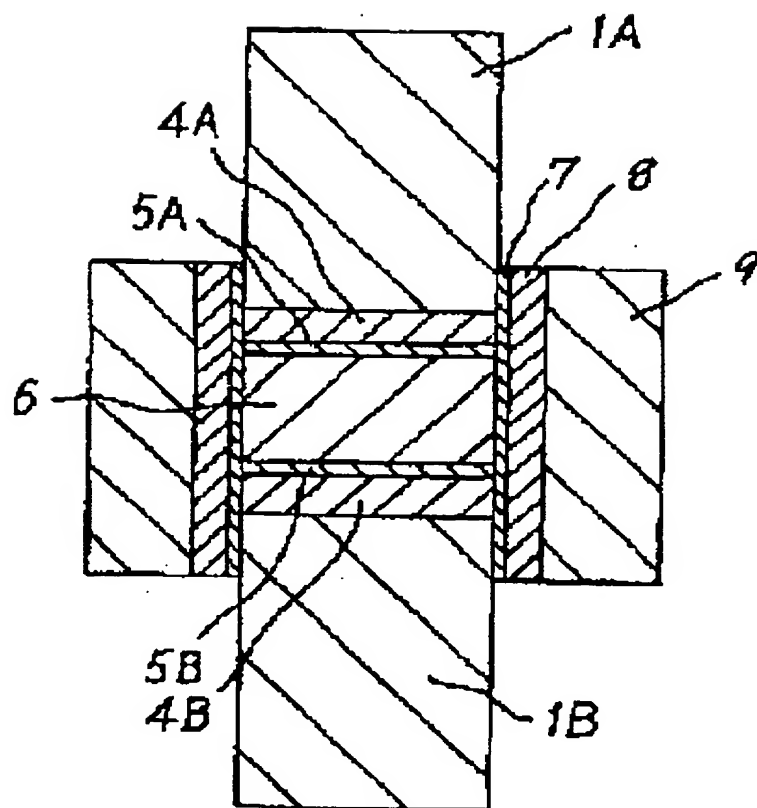


Fig.9

